PATENT COOPERATION TREATY

From the
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

To:

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PA 77674 HD

Ve, HD

PCT

WRITTEN OPINION
(PCT Rule 66)

Date of mailing *(day/month/year)*	18.05.2004
Applicant's or agent's file reference 77674 HD/Ve	**REPLY DUE** **within 2 month(s)** from the above date of mailing

International application No.	International filing date *(day/month/year)*	Priority date *(day/month/year)*
PCT/DK 03/00497	15.07.2003	16.07.2002

International Patent Classification (IPC) or both national classification and IPC
C23C8/22

Applicant
DANMARKS TEKNISKE UNIVERSITET-DTU et al.

1. This written opinion is the **first** drawn up by this International Preliminary Examining Authority.

2. This opinion contains indications relating to the following items:

   - I ☒ Basis of the opinion
   - II ☐ Priority
   - III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
   - IV ☐ Lack of unity of invention
   - V ☒ Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
   - VI ☐ Certain documents cited
   - VII ☐ Certain defects in the international application
   - VIII ☐ Certain observations on the international application

3. The applicant is hereby **invited to reply** to this opinion

   When? See the time limit indicated above The applicant may, before the expiration of that time limit, request this Authority to grant an extension, see Rule 66.2(d).

   How? By submitting a written reply, accompanied, where appropriate, by amendments, according to Rule 66 3. For the form and the language of the amendments, see Rules 66.8 and 66 9

   Also: For an additional opportunity to submit amendments, see Rule 66 4.
   For the examiner's obligation to consider amendments and/or arguments, see Rule 66 4 bis
   For an informal communication with the examiner. see Rule 66 6.

   If no reply is filed, the international preliminary examination report will be established on the basis of this opinion

4. The final date by which the international preliminary examination report must be established according to Rule 69.2 is: 16 11 2004

Name and mailing address of the international preliminary examining authority:	Authorized Officer
European Patent Office D-80298 Munich Tel +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Mizera, E Formalities officer (incl extension of time limits) Marchetto, L Telephone No +49 89 2399-2796

I. Basis of the opinion

1. With regard to the **elements** of the international application *(Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this opinion as "originally filed")*:

Description, Pages

1-12 as originally filed

Claims, Numbers

1-11 as originally filed

Drawings, Sheets

1/2, 2/2 as originally filed

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

   These elements were available or furnished to this Authority in the following language: , which is:

   - ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
   - ☐ the language of publication of the international application (under Rule 48.3(b)).
   - ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

   - ☐ contained in the international application in written form.
   - ☐ filed together with the international application in computer readable form.
   - ☐ furnished subsequently to this Authority in written form.
   - ☐ furnished subsequently to this Authority in computer readable form.
   - ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
   - ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

   - ☐ the description, pages:
   - ☐ the claims, Nos.:
   - ☐ the drawings, sheets:

5. ☐ This opinion has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)).

6. Additional observations, if necessary:

V. Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Claims	1-11
Inventive step (IS)	Claims	1-11
Industrial applicability (IA)	Claims	

2. Citations and explanations

see separate sheet

AS TO BOX V:

1. The following documents are cited:

   D1: NL-A-1 003 455 (RIJKSUNIVERSITEIT GRONINGEN TE GRONINGEN) 2 March 1998 (1998-03-02)
   D2: US-A-4 013 487 (RAMQVIST LARS H ET AL) 22 March 1977 (1977-03-22)
   D3: DATABASE WPI Section Ch, Week 198408 Derwent Publications Ltd., London, GB; Class M13, AN 1984-045734 XP002262970 & JP 59 006367 A (NICCHI KK), 13 January 1984 (1984-01-13)
   D4: EP-B-0 248 431 (POLITECHNIKA KRAKOWSKA ;SAMOCHODOW MALOLITRAZOWYCH POL (PL)) 9 December 1987 (1987-12-09)
   D5: DD 294 048 A (FREIBERG BERGAKADEMIE) 19 September 1991 (1991-09-19)
   D6: WO 01 55470 A (MARX STEVEN V ;SWAGELOK CO (US); WILLIAMS PETER C (US)) 2 August 2001 (2001-08-02)
   D7: WO 00 50661 A (MARX STEVEN V ;SWAGELOK CO (US); WILLIAMS PETER C (US)) 31 August 2000 (2000-08-31)

2. All of the cited documents anticipate the disclosure of method claim 1. Reference is made in particular to D1, claims 1, 4, 5 and 7, where conditions for the deposition of a catalytic layer of Ni, Co or Pd on top of the article to be treated are described. These conditions correspond to the conditions used in the present application. In claim 16 the activation of the surface of the article to be treated is mentioned.

3. With respect to this prior art claim 1 lacks novelty and an inventive step under Art.33(2) and (3) PCT. This applies also to dependent claims 2-10 and to claim 11.

4. As to claim 11 it is explicitly stated that product claims would not seem to meet the requirements of Art.6 PCT, as a claimed process can be carried out in many different ways, resulting in many different (and undefined!) products.

5. With respect to documents D2-D7, which equally anticipate the teaching of independent claims 1 and 11, reference is made to the passages cited in the

search report.

10/521612

Amended page of 9 July 2004

Title: Case-hardening of stainless steel

DT09 Rec'd PCT/PTO 14 JAN 2005

Technical Field

The present invention relates to a method according to the preamble of claim 1.

Background Art

Thermo-chemical surface treatments of steel by means of carbon or nitrogen carrying gases are well-known processes, called case-hardening or carburization or nitriding. Nitro-carburization is a process in which a gas carrying both carbon and nitrogen is used. These processes are traditionally applied to improve the hardness and wear resistance of iron and low alloyed steel articles. The steel article is exposed to a carbon and/or nitrogen carrying gas at an elevated temperature for a period of time, whereby the gas decomposes and carbon and/or nitrogen atoms diffuse through the steel surface into the steel material. The outermost material close to the surface is transformed into a layer with improved hardness, and the thickness of this layer depends on the treatment temperature and the treatment time.

Stainless steel has excellent corrosion properties, but is relatively soft and has poor wear resistance, especially against adhesive wear. Therefore, there is a need of improving the surface properties for stainless steel. Gas carburization, nitriding and nitro-carburizing of stainless steel involve some difficulties, as the passive layer, causing the good corrosion properties, acts as a barrier layer preventing carbon and/or nitrogen atoms from diffusing through the surface. Also the elevated temperatures of the treatments promote the formation of chromium carbides or chromium nitrides. The formation of chromium carbides and/or chromium nitrides reduces the free chromium content in the material whereby the corrosion properties are deteriorated.

process can be carried out at temperatures below 400°C, and the purpose is to obtain a pore-free iron nitride layer.

Disclosure of Invention

The object of the invention is to provide a new and improved method for case-hardening stainless steel. The object of the invention is obtained by a process according to the preamble of claim 1, wherein the top layer includes metal which is catalytic to the decomposition of the gas carrying the carbon or/and nitrogen atoms and which is one or more of the metals Ni, Ru, Co or Pd. The metal layer protects the stainless steel surface from oxidation and acts as a catalytic surface for the decomposition of the gas. As a result, the process temperature can be kept below the temperature at which carbides and/or nitrides are formed, and the process can be finished within a reasonable period of time. After the thermo-chemical treatment, the catalytic metal layer can be removed to expose and repassivate the hardened stainless steel surface.

When carbon atoms, nitrogen atoms or both diffuse into stainless steel, the metastable S-phase is formed. S-phase is also called "expanded austenite" and has carbon and/or nitrogen in a solid solution at an upper stable temperature of about 450°C when it is nitrogen-stabilized, and at about 550°C when it is carbon-stabilized. Thus, the process according to the invention can be carried out at temperatures up to 450°C or 550°C to obtain S-phase.

Until now, S-phase in stainless steel has almost only been obtained by plasma-assisted or ion implantation-based processes. Tests have established that the formation of S-phase at the surface does not negatively change the corrosion resistance of stainless steel. For nitrogen-stabilized S-phase an improvement of corrosion resistance can be obtained.

When stainless steel is treated with the method according to the invention, the hardness and wear resistance are improved considerably without the deterioration of the corrosion properties.

The ammonia synthesis, i.e. the production of NH_3 from H_2 and N_2, involves the use of a number of catalytic metals. Traditionally, the process is carried out at temperatures in the range 400°C – 700°C at high pressures (>300 atm) in the presence of a catalyst material. Gaseous nitriding is in principle the reverse process of the ammonia synthesis, where ammonia is dissociated on a metal surface producing N available for diffusion into the material to be nitrided. The conventional nitriding process is carried out within the same temperature interval as the ammonia synthesis process but at normal pressures. The catalytic metals available in the ammonia synthesis process are also found to promote the low-temperature catalytic reaction (ammonia dissociation) of the nitriding process. Known catalysts from the ammonia synthesis process include Fe, Ni, Ru, Co, Pd among others.

According to an embodiment of the invention, the case-hardening is a nitriding process which is carried out with a nitrogen containing gas below a temperature at which nitrides are produced, preferably below approximately 450°C.

EP 0248431 B1 discloses a method where an austenitic stainless steel article is electroplated with iron before nitriding at 575°C for 2 hours. As mentioned before, chromium nitrides are formed at this temperature. As disclosed on page 4, lines 13 to 18 of EP 0248431 B1, only the valve shaft of a valve is nitrided. The valve disk (Ventilteller) is protected from nitriding by an oxide layer in order not to reduce the corrosion resistance of the valve disk.

The same idea is followed with respect to carburizing, where the same catalytic metals are applicable also.

The material applied for the surface layer should include the well known materials from the ammonia synthesis process either as pure metals (single layer), as alloys, as a metal layer doped with other metals and as multi-layers.

Claims

1. A method of case-hardening a stainless steel article by means of gas including carbon and/or nitrogen, whereby carbon and/or nitrogen atoms diffuse through the surface of the article, the case-hardening is carried out below a temperature at which carbides and/or nitrides are produced, the method including activating the surface of the article, applying a top layer on the activated surface to prevent repassivation, the top layer includes metal which is catalytic to the decomposition of the gas, **characterised in that** the metal is one or more of the metals Ni, Ru, Co or Pd.

2. A method according to claim 1, wherein the case-hardening is a nitriding process which is carried out with a nitrogen-containing gas below a temperature at which nitrides are produced, preferably below approximately 450°C.

3. A method according to claim 1, wherein the case-hardening is carburizing with a carbon-containing gas, preferably CO.

4. A method according to claim 3, wherein carburizing is carried out below a temperature at which carbides are produced, preferably below approximately 550°C, more preferably below approximately 510°C.

5. A method according to any of the preceding claims, wherein the top layer is a nickel layer.

6. A method according to claim 5, wherein the maximum average thickness of the nickel layer is 300 nanometer, preferably 200 nanometer.

7. A method according to claim 5 or 6, wherein the nickel layer is applied by a chemical or electrolytical plating process, e.g. by electro-plating in a Wood's nickel bath.

8. A method according to any of the preceding claims, wherein the article is of austenitic stainless steel.

9. A method according to any of the preceding claims, wherein the catalytic metal layer is only applied to parts of the surface of the stainless steel article.

DRAFT AMENDMENTS JULY 2004

DT09 Rec'd PCT/PTO 14 JAN 2005

Title: Case-hardening of stainless steel

Technical Field

The present invention relates to a method according to the preamble of claim 1. ~~and a stainless steel article according to claim 11.~~

Background Art

Thermo-chemical surface treatments of steel by means of carbon or nitrogen carrying gases are well-known processes, called case-hardening or carburization or nitriding. Nitro-carburization is a process in which a gas carrying both carbon and nitrogen is used. These processes are traditionally applied to improve the hardness and wear resistance of iron and low alloyed steel articles. The steel article is exposed to a carbon and/or nitrogen carrying gas at an elevated temperature for a period of time, whereby the gas decomposes and carbon and/or nitrogen atoms diffuse through the steel surface into the steel material. The outermost material close to the surface is transformed into a layer with improved hardness, and the thickness of this layer depends on the treatment temperature and the treatment time.

Stainless steel has excellent corrosion properties, but is relatively soft and has poor wear resistance, especially against adhesive wear. Therefore, there is a need of improving the surface properties for stainless steel. Gas carburization, nitriding and nitro-carburizing of stainless steel involve some difficulties, as the passive layer, causing the good corrosion properties, acts as a barrier layer preventing carbon and/or nitrogen atoms from diffusing through the surface. Also the elevated temperatures of the treatments promote the formation of chromium carbides or chromium nitrides. The formation of chromium carbides and/or chromium nitrides reduces the free chromium content in the material whereby the corrosion properties are deteriorated.

process can be carried out at temperatures below 400°C, and the purpose is to obtain a pore-free iron nitride layer.

Disclosure of Invention

The object of the invention is to provide a new and improved method for case-hardening stainless steel. The object of the invention is obtained by a process according to the preamble of claim 1, wherein the top layer includes metal which is catalytic to the decomposition of the gas carrying the carbon or/and nitrogen atoms <->. The metal layer protects the stainless steel surface from oxidation and acts as a catalytic surface for the decomposition of the gas. As a result, the process temperature can be kept below the temperature at which carbides and/or nitrides are formed, and the process can be finished within a reasonable period of time. After the thermochemical treatment, the catalytic metal layer can be removed to expose and repassivate the hardened stainless steel surface.

When carbon atoms, nitrogen atoms or both diffuse into stainless steel, the metastable S-phase is formed. S-phase is also called "expanded austenite" and has carbon and/or nitrogen in a solid solution at an upper stable temperature of about 450°C when it is nitrogen-stabilized, and at about 550°C when it is carbon-stabilized. Thus, the process according to the invention can be carried out at temperatures up to 450°C or 550°C to obtain S-phase.

Until now, S-phase in stainless steel has almost only been obtained by plasma-assisted or ion implantation-based processes. Tests have established that the formation of S-phase at the surface does not negatively change the corrosion resistance of stainless steel. For nitrogen-stabilized S-phase an improvement of corrosion resistance can be obtained.

<and which is one or more of the metals Ni, Ru, Co or Pd>

When stainless steel is treated with the method according to the invention, the hardness and wear resistance are improved considerably without the deterioration of the corrosion properties.

The ammonia synthesis, i.e. the production of NH_3 from H_2 and N_2, involves the use of a number of catalytic metals. Traditionally, the process is carried out at temperatures in the range 400°C – 700°C at high pressures (>300 atm) in the presence of a catalyst material. Gaseous nitriding is in principle the reverse process of the ammonia synthesis, where ammonia is dissociated on a metal surface producing N available for diffusion into the material to be nitrided. The conventional nitriding process is carried out within the same temperature interval as the ammonia synthesis process but at normal pressures. The catalytic metals available in the ammonia synthesis process are also found to promote the low-temperature catalytic reaction (ammonia dissociation) of the nitriding process. Known catalysts from the ammonia synthesis process include Fe, Ni, Ru, Co, Pd among others.

~~According to an embodiment, the top layer includes one or more of the metals Fe, Ni, Ru, Co or Pd.~~

According to an embodiment of the invention, the case-hardening is a nitriding process which is carried out with a nitrogen containing gas below a temperature at which nitrides are produced, preferably below approximately 450°C.

EP 0248431 B1 discloses a method where an austenitic stainless steel article is electroplated with iron before nitriding at 575°C for 2 hours. As mentioned before, chromium nitrides are formed at this temperature. As disclosed on page 4, lines 13 to 18 of EP 0248431 B1, only the valve shaft of a valve is nitrided. The valve disk (Ventilteller) is protected from nitriding by an oxide layer in order not to reduce the corrosion resistance of the valve disk.

The same idea is followed with respect to carburizing, where the same catalytic metals are applicable also.

The material applied for the surface layer should include the well known materials from the ammonia synthesis process either as pure metals (single layer), as alloys, as a metal layer doped with other metals and as multi-layers.

~~As an example, a stainless steel article could be provided with an iron layer and a very thin ruthenium layer on the top of the iron layer.~~

Claims

1. A method of case-hardening a stainless steel article by means of gas including carbon and/or nitrogen, whereby carbon and/or nitrogen atoms diffuse through the surface of the article, [ ] the method including activating the surface of the article, applying a top layer on the activated surface to prevent repassivation, **characterised in that** the top layer includes metal which is catalytic to the decomposition of the gas, the metal is

H dl
U dl ~~2. A method according to claim 1, wherein the top layer includes~~ one or more of the metals Fe, Ni, Ru, Co or Pd.

Hdl ~~3~~ 2. A method according to claim 1 ~~or 2~~, wherein the case-hardening is a nitriding process which is carried out with a nitrogen-containing gas below a temperature at which nitrides are produced, preferably below approximately 450°C.

H dl
H dl ~~4~~ 3. A method according to claim 1 ~~or 2~~, wherein the case-hardening is carburizing with a carbon-containing gas, preferably CO. ~~and where the top layer is free of Fe~~

~~5~~ 4. A method according to claim ~~4~~ 3, wherein carburizing is carried out below a temperature at which carbides are produced, preferably below approximately 550°C, more preferably below approximately 510°C.

~~6~~ 5. A method according to any of the preceding claims, wherein the top layer is a nickel layer.

~~7~~ 6. A method according to claim ~~6~~ 5, wherein the maximum average thickness of the nickel layer is 300 nanometer, preferably 200 nanometer.

~~8~~ 7. A method according to claim ~~6~~ 5 or ~~7~~ 6, wherein the nickel layer is applied by a chemical or electrolytical plating process, e.g. by electro-plating in a Wood's nickel bath.

[the case-hardening is carried out below a temperature at which carbides and/or nitrides are produced,]

8 ~~9~~. A method according to any of the preceding claims, wherein the article is of austenitic stainless steel.

9 ~~10~~. A method according to any of the preceding claims, wherein the catalytic metal layer is only applied to parts of the surface of the stainless steel article.

~~11. A stainless steel article treated by a method according to any of the preceding claims.~~